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(12) UK Patent (19) GB (11) 2 178 746 (13) B

(54) Title of Invention

Clouded plastics elements

(51) INT CL<sup>4</sup>; C08L 33/04 // G03B 21/56

(21) Application No  
8619183

(22) Date of filing  
6 Aug 1986

(30) Priority data

(31) 3528165

(32) 6 Aug 1985

(33) Fed. Rep. of Germany  
(DE)

(43) Application published  
18 Feb 1987

(45) Patent published  
1 Feb 1989

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(52) Domestic classification  
(Edition J)  
C3M 107 136 145 146 152  
153 155 165 300 C  
U1S 2226 3038 3069 3070  
3073 C3M

(56) Documents cited  
GB 1370785  
US 4464513

(58) Field of search  
C3M  
C3V

Clouded plastics elements

The present invention relates to clouded plastics elements. More particularly it relates to shaped and flat plastics elements comprising inherently transparent plastics which are particularly suitable  
5 as light projection screens e.g. as television projection screens.

Various technical tasks can only be performed by using partly transparent glass. These tasks include  
10 the job of making glass matt and the manufacture of projection screens and other optical display elements.

As a rule, use is made of light refraction or light  
15 scattering at phase limits, such as occurs, for example, when particles of suitable dimensions are embedded as a dispersed phase in a carrier phase and the two phases have different refractive indices. The carrier phase advantageously consists  
20 of for example, plastics. Manufacturers active in this field have developed, as well as inorganic particles such as glass beads, polymer particles suitable for embedding in the carrier phase.

25 Thus, for example, DE-A-21 46 628 discloses a method of polymerisation for preparing finely divided polymer particles, in which a monomer system (A) is prepared, which is capable of free radical addition polymerisation and which contains

30

87 to 99.99% by weight of a monoethylenically unsaturated monomer and  
0.01 to 3% by weight of at least one polyunsaturated monomer, and

5 to 50% by weight, based on the total mixture,  
of a different soluble thermo-  
plastic addition polymer  
is totally dissolved in  
5 the monomer system (A),  
the first polymer being  
insoluble in the thermoplastic  
polymer; and  
the solution of the two is subjected to conditions  
10 under which the monomer system undergoes free radical  
polymerisation forming substantially spherical  
cross-linked polymer particles, having an average  
particle size in the range from 0.5 to 30 microns,  
these particles being dispersed in a continuous  
15 phase of the thermoplastic polymer.

The polymer particles which are formed according  
to DE-A-21 46 628 are cross-linked and are therefore  
scarcely capable of fusion and deformation, with  
20 the result that they can be compressed with powders,  
for example, or subjected to injection moulding.

In the form of a solution, the polymer formed according  
to this citation may, for example, be sprayed onto  
25 acrylic resin sheets. The citation mentions the  
possibility of using the polymer as a dulling lacquer  
and in the form of mixtures which are suitable  
for the manufacture of optical screens with backwards  
projection and in computers, in the television  
30 and film industries, in photography, etc.

DE-A-21 46 607 also discloses translucent to opaque  
plastics mixtures which contain spherical cross-  
linked particles of addition polymer consisting  
35 of 87-99.99% by weight of at least one monoethylenically  
unsaturated monomer and 0.01 to 3% by weight of  
a monomeric cross-linker dispersed in a continuous

phase of an addition polymer, the addition polymer being soluble in the mixed monomers. The plastics mixture preferably also contains additional copolymerised cross-linking agent. Possible fields of application mentioned in this citation are self-supporting translucent plastics sheets, strips of film and the like. When a solution of the polymeric material is sprayed onto acrylic films, matt films are obtained. The mixtures are also supposed to be suitable for image screens with backward projection.

JP-A-80 93102 (Chem. Abstr. 93, 240792y) describes light-scattering acrylic resin sheets which are obtained by belt polymerisation from acrylic resin film and acrylate monomers which contain a light-scattering agent in sandwich configuration.

JP-A-81 117 225 (Chem. Abstr. 96, 86627b) discloses optical screens which have a broad light diffusing effect in one direction and act as optical lenses in the other direction. The screens according to JP-A-81 117 225 are produced by embedding powdered glass fibres in modified acrylic resin and subsequently carrying out monoaxial stretching, followed by a final coating with an acrylate layer containing carbon black. Light-scattering acrylic resin sheets used as projection screens are the subject of JP-A-82 05742 (Chem. Abstr. 96, 200768a), in which the desired light scattering is achieved by means of quartz pellets 0.5 to 20 microns in diameter embedded in PMMA (polymethylmethacrylate). According to British Patent 1 585 338, light-scattering sheets with better optical resolution, greater optical half-power angles and greater flexibility than conventional sheets containing glass fibres are obtained by using plastics sheets filled with glass beads. The glass beads have diameters of from

0.001 to 0.05 mm. Examples of carrier materials mentioned are thermoplastics such as cellulose esters, polycarbonate, polyarylsulphone, polystyrene and acrylic resins.

5 The solutions in the prior art concerning "translucent to opaque plastics mixtures and the use thereof, for example, in the manufacture of sheet or film material" have not proved entirely satisfactory. In particular, requirements have not been fully  
10 met with regard to suitability as optical projection screens. It was also desirable that the material should be extrudable without any serious technical disadvantages.

We have now found that certain clouded, particularly  
15 shaped flat plastics elements satisfy the demands made of optical projection screens, especially television projection screens, to an exceptional degree if cross-linked bead-polymerised beads are incorporated into a polymer matrix (PM) in an amount of from  
20 1 to 30% by weight, based on the polymer matrix (PM), these cross-linked beads being formed of polymer P which comprises

9.9 to 59.9% by weight of one or more radically  
polymerisable monomers A  
which contain an aromatic  
25 group or non-aromatic monomers  
A' which contain halogen,  
and  
90 to 40% by weight of vinyl monomers B which  
are copolymerisable with  
30 said monomers A and A' but  
different from them, and  
0.1 to 20% by weight of at least one cross-linking  
monomer V,

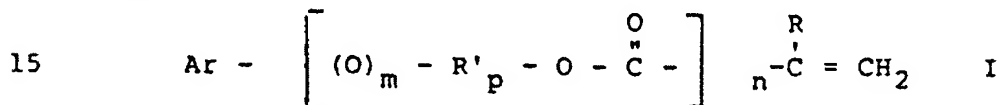
with the proviso that

- a) the refractive index of the polymer P is higher than that of the polymer matrix and
- 5 b) the average bead size of the beads is 5 to 50 microns, preferably 10 to 35 microns.

Polymer P may also contain from 0 to 10% by weight of a (strongly) polar monomer H.

10

Examples of radically polymerisable monomers A which contain an aromatic group are monomers of formula I



- wherein Ar represents an optionally substituted aromatic hydrocarbon group with up to 12 carbon atoms, preferably an aromatic group optionally
- 20 substituted with C<sub>1-4</sub> alkyl groups or with fluorine, chlorine or bromine or both types of substituent, more particularly a phenyl group,
- R represents hydrogen or methyl,
- R' represents an optionally branched alkylene
- 25 group with 1 to 8 carbon atoms,
- n represents zero or one,
- m represents zero or one, and
- p represents zero or one, with the proviso that if p represents zero, m must also represent
- 30 zero.

Homo- and copolymers formed solely from monomers of formula I generally have a refractive index N<sub>d</sub> of more than 1.56.

- 35 Preferably, the monomers of formula I are styrene and/or the methyl-substituted derivatives thereof such as α-methylstyrene and p-methylstyrene, p-

ethylstyrene and halogenated derivatives of styrene such as p-chlorostyrene. Other examples of monomers A of formula I include phenylacrylate and -methacrylate, xylylenemethacrylate and -acrylate, particularly  
 5 the m-form, 4-methylphenylacrylate and -methacrylate, 2-phenylethylacrylate and -methacrylate, 3-phenyl-1-propylmethacrylate and -acrylate, and 2-phenyloxyethyl-acrylate and -methacrylate.

10 Of the non-aromatic monomers A' which contain halogen, preferred are those which contain, in particular, chlorine or bromine in a non-activated and therefore readily hydrolysable bond, for example the α-chloro- and α-bromoacrylic and -methacrylic acid esters  
 15 of C<sub>1-6</sub> alcohols such as methyl-α-chloroacrylate and also vinyl chloride and vinylidene chloride.

Of the copolymerisable vinyl monomers B, preferred are those of formula .II

20



wherein R represents hydrogen or methyl and R''  
 25 represents an optionally branched, optionally cyclic alkyl group with 1 to 8 carbon atoms, whilst the cyclic alkyl groups preferably have at least 5 cyclic carbon atoms. Various examples of monomers of groups A, B and C may be used provided that  
 30 their activity corresponds to the features specified. Homo- and copolymers formed solely from monomers of formula II generally have a refractive index  $n_D$  of < 1.51, generally less than 1.49.

35 The vinyl monomers B are preferably chosen so that the resulting glass temperature  $T_g$  (measured by dilatometry) of a polymer or copolymer prepared

therefrom would be at least 80°C. (For the  $T_g$  and the contributions of the monomers, see Brandrup-Immergut and B. Vieweg, F. Esser, in the *Plastics Handbook*, Volume IX, Hanser-Verlag 1975, pages 5 333 to 340; T.G. Fox *Bull. Am. Phys. Soc.* 1, 125, 1956).

It is particularly preferred that the vinyl monomer B should consist either wholly or to an extent 10 of at least 40% by weight of methylmethacrylate.

Of the cross-linking monomers V, preferred are the known radical cross-linkers. The cross-linking monomers usually have more than one radically polymerisable 15 unit in the molecule. Mention should be made of those with two vinyl groups such as divinylbenzene, also acrylic and methacrylic acid esters and amides of polyols such as glycoldi(meth)acrylate, 1,3- and 1,4-butanediol(meth)acrylate, trimethylolpropanetri- 20 (meth)acrylate, tetraethyleneglycoldi(meth)acrylate, and so on, and also monomers which contain vinylidene, the (hidden) amide methylol, carbamide methylolether, azlactone and epoxy groups, such as N-methylol(meth)-acrylamide, methylenebisacrylamide and -methacrylamide, 25 glycidyl(meth)acrylate, and particularly also cross-linking monomers with unsaturated groups of graduated reactivity in the molecule such as the vinyl, allyl and crotylestere of acrylic and/or methacrylic acid. (Cf. H. Rauch-Puntigam, Th. Völker, *Acrylic and Methacrylic Compounds*, Springer-Verlag Berlin, 30 1967).

Cross-linking is intended to ensure that the beads do not fuse during processing at elevated temperature 35 (up to about 300°C).

Bead polymers may be prepared in known manner by

the process of bead polymerisation. In this process, monomers A, B and V, as a dispersed phase, are generally distributed by mechanical force (agitation) in a non-solvent (continuous phase) and polymerised  
5 in this form. The polymer formed is predominantly soluble in the monomer. Under the effect of interfacial tension the monomer forms spherical drops. In order to obtain this droplet shape during polymerisation and prevent the drops from running together, so-called "dispersers" or distributors (protective  
10 colloids) are added to the polymerisation mixture, preferably substances which can be totally removed from the bead polymer after polymerisation is complete.

15 The "distributor" ensures that, once formed, the droplets of monomer are stabilised so that it is virtually impossible for the drops to join together.

Water is generally used as the continuous phase.  
20 Therefore, primarily sparingly soluble to water-insoluble radically polymerisable monomers are used as the monomers suitable for polymerisation. (Cf. Houben-Weyl, 4th Edition, Volume XIV/1 "Macromolecular substances", pages 406 to 433, G. Thieme-Verlag  
25 1961).

Suitable distributors include (water-insoluble) salts of inorganic acids such as barium sulphate or barium carbonate or high molecular natural substances  
30 or synthetic polymers. The group of high molecular distributors includes water-soluble colloids such as polyvinyl alcohol, partially saponified polyvinylacetate, methylcellulose, starch, gelatine, pectin, the alkali metal salts of polyacrylic acid or the alkali  
35 metal salts of styrene or vinylacetate-maleic anhydride copolymers and the like (cf. Houben-Weyl, loc.cit, page 411 - 430). The ratio of aqueous to monomeric

phase is generally from 2:1 to 4:1. In bead polymerisation, as is well known, starters are used which are, in a first approximation, soluble in the monomer but insoluble in water. As a rule, the quantity of starter used is from 0.1 to 1% by weight, preferably around 0.5% by weight based on the monomers. Suitable starters include the conventional organic peroxides or corresponding azo compounds which are soluble in the monomer, such as dibenzoylperoxide, lauroylperoxide and azoisobutyronitrile. Radical forming agents with fairly high temperatures of decomposition may additionally be used if the temperature is increased towards the end of the reaction in order to achieve the maximum possible polymerisation. The bead size can be adjusted between 5 and 50 microns within the scope claimed.

Moreover, if desired, regulators such as the conventional sulphur regulators, e.g. aliphatic mercaptans such as laurylmercaptan and tert.dodecylmercaptan may be added to the bead polymerisation mixture. The average molecular weight  $M_w$  of the polymer P according to the invention if it were not cross-linked would generally be in the range from 1 to  $2 \cdot 10^5$  g/mol; a figure of about  $10^5$  g/mol should be taken as an approximate value ( $M_w$  determined by gel permeation chromatography).

It is also possible to add conventional lubricants such as fatty alcohols, stearic acid esters, palmitic acid esters or natural waxes, preferably before polymerisation.

A practical method of preparation may consist of first putting in the water, the monomers A, B and V, the starter dispersant and optionally lubricant

and then heating the mixture, for example to about 90°C. If necessary, the excess heat of polymerisation, particularly upwards of 95°C, is removed by external cooling.

- 5 The temperature will generally not exceed 115°C. The duration of polymerisation is usually in the range from 1 to 5 hours. The viscosity of the polymerisation mixture (measured with a Brookfield Viscosimeter) is generally in the range between  
10 8000 and 800 Centipoise.

The partly reactive lubricants are preferably only added after about 20% conversion. Regulators may also be added in the course of polymerisation.

- After the end of the reaction the beads are generally  
15 separated off by filtering or centrifuging. Any additives adhering to them can be eliminated by any suitable means, for example by washing with dilute acid and water. The beads are frequently dried with heating, preferably with air circulating  
20 round them, e.g. in rack dryers.

The polymer matrix PM to which the pearls are added is generally a transparent, usually thermoplastic synthetic material such as those which have already caught on in the art for the purpose of light projection.

- 25 The ratio of P to PM is most desirably determined, inter alia, by the fact that the difference between the refractive indices  $n_D$  (beads) minus  $n_D$  (polymer matrix) should be at least 0.01, preferably 0.04.

- Suitable plastics for the polymer matrix include  
30 polystyrenes, PVC, polyvinylacetate, polycarbonate, polyolefins and, in particular, acrylic resins.

The term "acrylic resins" within the scope of this invention refers to polymers which are made up of at least 50% by weight of monomeric esters of acrylic and/or methacrylic acid, particularly of  
5 the same type as formula II.

In order to prepare the clouded plastics elements according to the invention, the beads consisting of the polymer B must be incorporated in the polymer matrix and then distributed therein.

10 It is particularly surprising that we have succeeded in introducing the beads in the course of processing the polymer matrix PM with the aid of extruders. The beads are added to the extruder melt.

It was unexpected that a) the beads would retain  
15 their shape under the temperature and shearing conditions of extrusion and b) it would be possible to achieve the homogeneous distribution of the beads which is absolutely essential for the desired light scattering effect. Moreover, surprisingly,  
20 the jump in refractive indices at the interfaces between the polymer matrix PM and the polymer beads, which was also necessary to give the required light scattering effect, was achieved. There was a danger that this jump in the pattern of the refractive  
25 index at the above-mentioned interfaces would be "evened out" by diffusion processes - as occurs, for example, when the beads are introduced into polymerisable monomers - which would result in an undesirable change in the scattering effect.

The invention will be illustrated by the following non-limiting examples:

5 Example 1: Bead Polymerisation:

In a 100l vessel made of V4A steel and equipped with a nitrogen inlet and an Impeller stirrer 600g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and 6g of sodium paraffin sulfonate (trade mark STATEXAN of Bayer, Leverkusen) are  
10 dissolved in 50l of deionised water at 85°C and with stirring at 350rpm. The aluminium compound used as dispersant is precipitated by adding 264g of sodium carbonate. Subsequently a monomer mixture  
15 0.1kg of glycol dimethacrylate and 0.2kg of dilauroyl peroxide is added under nitrogen. Polymerisation is carried out at 80°C for 140 minutes and subsequently at 90°C for 60 minutes with continued stirring.

After cooling to 50°C the polymerisation mixture  
20 is treated with 600ml of sulphuric acid (50%) to dissolve the dispersant. The bead material is collected on a filter funnel, washed with deionised water and dried on hurdles for 20 hours at 50°C. The average size of the beads (medium value) thus  
25 produced is 37 microns and the refractive index of the beads is found to be 1.53.

Example 2: Production of Light Dispersing Plates by Extrusion:

30 (see Kirk-othmer, 3rd. ed. Vol 18, pages 185-190, ibid, Vol 15, pages 632-637).

In a twin cone-and-screw mixer 96.5 parts by weight of polymethylmethacrylate (PMMA) moulding material

(trade mark PLEXIGLAS 7N of Röhm GmbH) are mixed, optionally with the addition of adhesion promoters as conventionally used in the art. The mixture is extruded in a single screw extruder with degassing  
5 at a material temperature of 245°C to yield plates 3mm thick. These plates meet fully the requirements with regard to light dispersion and mechanical properties.

Alternatively, the beads may be added to the extruder melt with excellent results.

Transmission (= ratio of transmitted brightness to incident illumination) = 87-89%.

Half brightness angle (angle at which brightness is one half of maximum transmitted brightness) =  $8 \pm 1.5^\circ$ .

Claims

1. Clouded plastics elements which comprise a polymer matrix (PM) into which cross-linked bead-polymerised beads in an amount of from 1 to 30% by weight, based on the polymer matrix (PM), have been incorporated, said cross-linked beads being formed of polymer P which comprises

9.9 to 59.9% by weight of one or more radically polymerisable monomers A which contain an aromatic group or non-aromatic monomers A' which contain halogen and  
10 90 to 40% by weight of vinyl monomers B which are copolymerisable with monomers A and A' but  
15 are different from them and  
0.1 to 20% by weight of at least one cross-linking monomer V,

with the proviso that

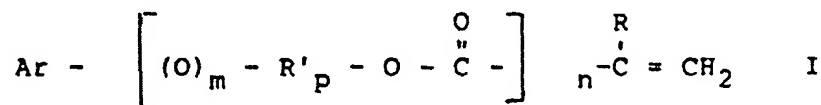
- 20 a) the refractive index of the polymer P is higher than that of the polymer matrix (PM) and that  
b) the average bead size of the beads is 5 to 50 microns.

25 2. Clouded plastics elements as claimed in claim 1 wherein polymer P includes from 0 to 10% of a polar monomer H.

3. Clouded plastics elements as claimed in claim

1 or claim 2 wherein the average bead size of the beads is 10 to 35 microns.

4. Clouded plastics elements as claimed in any of claims 1 to 3 wherein the radically polymerisable monomers A which contain an aromatic group are monomers of formula I



wherein Ar represents an optionally substituted aromatic hydrocarbon group with up to 12 carbon atoms,

- 10 R represents hydrogen or methyl,  
 R' represents an optionally branched alkylene group with 1 to 8 carbon atoms,  
 n represents zero or one,  
 m represents zero or one, and  
 15 p represents zero or one, with the proviso that if p represents zero, m must also represent zero.

5. Clouded plastics elements as claimed in any one of claims 1 to 4 wherein

- 20 Ar represents an aromatic group optionally substituted with C<sub>1-4</sub> alkyl groups or with fluorine, chlorine or bromine or both types of substituent, more particularly a phenyl group,

and R, R', n, m and p are as defined in claim 4.

- 25 6. Clouded plastics elements as claimed in any one of claims 1 to 5 wherein the monomers of formula I (as defined in claim 4) are styrene and/or the methyl-substituted derivatives thereof.

7. Clouded plastics elements as claimed in any one of claims 1 to 6 wherein the copolymerisable vinyl monomers B are those of formula II



- 5 wherein R represents hydrogen or methyl and R'' represents an optionally branched, optionally cyclic alkyl group with 1 to 8 carbon atoms, whilst the cyclic alkyl groups preferably have at least 5 cyclic carbon atoms.
- 10 8. Clouded plastics elements as claimed in any one of claims 1 to 7 which are produced by adding the cross-linked beads in metered amounts to the melt of the polymer matrix PM in the course of an extrusion process.
- 15 9. Clouded plastics elements as claimed in claim 1 substantially as herein described.
10. A process for the preparation of clouded plastics elements as defined in claim 1 comprising incorporating beads produced by bead polymerisation in aqueous  
20 media and isolated therefrom into said polymer matrix.
11. A process as claimed in claim 10 wherein said beads produced by bead polymerisation in aqueous media and isolated therefrom are incorporated into said polymer matrix in a molten state in an extruder  
25 and said mixture is extruded.
12. A process as claimed in claim 10 substantially as herein described.
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